

May 8, 1890.

Sir G. GABRIEL STOKES, Bart., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read:—

- I. "On certain Ternary Alloys. Part II." By C. R. ALDER WRIGHT, D.Sc., F.R.S., Lecturer on Chemistry and Physics, and C. THOMPSON, F.C.S., F.I.C., Demonstrator of Chemistry, in St. Mary's Hospital Medical School. Received April 3, 1890.

In Part I, it has been shown that when the three metals lead, zinc, and tin are fused together and well intermixed, and the mixture allowed to stand molten for some hours at a nearly constant temperature, a single homogeneous alloy results if the proportion of tin present exceeds a certain limiting amount (about three-eighths of the entire mass); but with smaller proportions of tin the mass divides itself into two different ternary alloys of unequal density: the heavier contains chiefly lead, together with some of the tin, and as much zinc as the lead can dissolve in presence of the particular proportion of tin associated with it; whilst the lighter mainly consists of zinc, with the rest of the tin, and as much lead as the zinc can dissolve in presence of that tin.

We have found that analogous results are obtained with various other ternary mixtures of metals, A, B, C, such that whilst A and B are not miscible together in all proportions (like lead and zinc), C is miscible in all proportions with either A or B separately. Of such mixtures, the following are examples:—

Heavier metal, A.	Lighter metal, B.	Third metal, C.
Lead.	Zinc.	Tin.
Lead.	Zinc.	Silver.
Lead.	Zinc.	Cadmium.
Lead.	Zinc.	Antimony.
Bismuth.	Zinc.	Tin.
Bismuth.	Zinc.	Silver.
Lead.	Aluminium.	Tin.
Lead.	Aluminium.	Silver.
Bismuth.	Aluminium.	Tin.
Bismuth.	Aluminium.	Silver.

We have made a large number of experiments with various mixtures of this kind. So far as our results are completed, they lead to the following general conclusions:—

1. In all cases, the mixture of the three metals A, B, C, when allowed to stand molten for a sufficient length of time at a tolerably equable temperature, divides itself into two different ternary alloys of unequal density, if the proportion of C present in the entire mass falls below a certain limiting amount; but, if the quantity of C present is above this limit, no such separation takes place, only one homogeneous alloy resulting.

2. Under ordinary circumstances, the different alloys thus formed are respectively a saturated solution of A in a mixture of B and C (lighter alloy), and one of B in a mixture of A and C (heavier alloy); the solubilities being such that, the greater the proportion of C present, the more of A (or B) is dissolved. Certain metals, however, appear to be capable of forming true chemical compounds in atomic proportion, in which case the quantity of A (or B) dissolved does not always vary directly with the amount of C present.

3. The quantity of B dissolved by a given weight of A (or of A dissolved by a given weight of B) in presence of a given weight of C varies considerably with the nature of C. Moreover, although in certain cases (*e.g.*, the lead-zinc-tin alloys examined in Part I) a considerable variation in temperature makes hardly any measurable difference in the solubility, this is very far from being the general rule; the ordinary effect of increment in temperature is to increase the solubility of A in BC, and of B in AC, in some cases to a very considerable extent.

4. The third metal C divides itself between the two alloys in a fashion variable not only with the nature of A, B, and C, and with the temperature, but also with the relative proportions subsisting between A and B in the entire mass, and with the proportions of C contained therein. If curves be drawn, as described in Part I, with the percentages of C in one alloy as abscissæ and the differences in percentage between the two alloys as ordinates, two classes of curves may be distinguished. In one, the percentage in the lighter alloy is greater than that in the heavier; calling the difference +, the curve *rises* from the origin above the base line. In the other, the percentage in the lighter alloy is less than that in the heavier one; so that the difference is now —, and the curve *falls* from the origin below the base line. With curves of the first kind, it generally happens that the ordinate value increases gradually to a maximum and then diminishes; with some metals (*e.g.*, silver-lead-zinc) the diminution is only just perceptible; with others (*e.g.*, silver-bismuth-zinc) it is more marked; whilst with some (*e.g.*, tin-lead-zinc) it is carried so far that at length the ordinate becomes 0, and subsequently — in

sign, *i.e.*, the curve first rises above the base line to a maximum, and then sinks again, and crosses the base line, falling below it. Similarly, with curves of the second kind, it sometimes happens that the ordinate value reaches a negative maximum, and then lessens again, so that the curve again approaches the base line; as yet, however, we have not met with a case where the curve actually crosses the line giving a + ordinate value.

Mixtures of Lead, Zinc, and Tin at Higher Temperatures.

The experiments described in Part I indicated that little if any difference is produced in the composition of the two alloys into which a given mass of these three metals separates by varying the temperature at which the fused mass is maintained between 565° and 689°, or between about 650° and 750°; sensibly the same solubility curves for zinc in lead-tin, and for lead in zinc-tin, resulting in all cases. We find, however, that if a higher temperature be employed, 750—850° and upwards, a measurable increment in solubility is produced. At this more elevated temperature, the volatility of zinc is considerably enhanced, so that the ratio between the lead and zinc present in the compound ingot finally obtained differs more from that in the mass of metals originally weighed up than was the case in the experiments described in Part I; in those experiments, the average loss by oxidation and volatilisation per 100 parts of original metals jointly was nearly 4 parts, of which scarcely anything was due to loss of tin, about one-third to loss of lead, and some two-thirds to loss of zinc. In the experiments described below, 100 parts of original metals lost on an average about 10 or 12 parts altogether, almost the entire increment in the loss being due to enhanced volatilisation of zinc, this larger amount being due not only to the higher temperature, but also to the longer time of fusion (some twenty-four hours instead of eight). To reduce this loss by volatilisation to a minimum, the molten metals, when poured into the red-hot narrow clay test-tubes, were covered with layers of fused cyanide of potassium some 12 or 15 millimetres thick.

The melting arrangements employed throughout in the experiments described in this paper were substantially those detailed in Part I: *viz.*, the weighed metals were fused with cyanide of potassium in a clean crucible, well stirred together for some time, and poured into a red-hot clay test-tube, which was then kept hot for some hours by immersion in a bath of molten lead, fused in an iron cylindrical vessel surrounded by a clay jacket, several large Bunsen flames playing into the interspace being the source of heat. The temperature was ascertained from time to time by means of the platinum specific heat pyrometer, as described in Part I. It was

found more convenient to surround the clay test-tubes with thin wrought iron coverings made of wider tubes closed at the end; by so doing, the chance of spoiling an experiment by the infiltration of lead from the bath through minute cracks in the clay was avoided; moreover, by simply removing from the iron tubes the inner clay test-tubes by means of tongs, a new set of test-tubes containing fused mixtures could be readily introduced into the lead-bath without extinguishing the heating flames; whereas, when the clay test-tubes were plunged directly into the molten lead, the layer of fritted litharge that formed on the outer surface of the lead-bath sometimes rendered it difficult to remove the clay tubes without agitation.

Somewhat smaller ingots than those previously used were mostly prepared, usually weighing 50—60 grams, instead of 80 and upwards; the compound ingots ultimately formed were generally about 7 or 8 centimetres long, and 10—12 millimetres diameter.

The following solubility values for pure lead in pure zinc, and *vice versa* (no tin being present), were obtained in a number of different observations.

Percentage of Zinc in Heavier Alloy.

At 565—750° (Part I).	At 750—850°.
1·14	1·23
1·22	1·27
1·30	1·28
1·30	1·34
	1·35
	1·36
Mean....1·24	Mean....1·30

Percentage of Lead in Lighter Alloy.

At 565—750° (Part I).	At 750—850°.
1·08	1·40
1·10	1·57
1·17	1·64
1·22	1·67
Mean....1·14	Mean....1·57

It hence results that the solubility of zinc in lead is greater at a temperature near to an average of 800° than at one near to an average of 650° by an amount only just perceptible, and barely outside the limits of experimental error; whilst the solubility of lead in zinc is increased nearly in the proportion of 3 to 2 by the same

temperature increment. The values described below show that when tin is also present the increment in solubility with higher temperature is in each case well marked.

The following mean values were obtained from twelve compound ingots, prepared by fusion for twenty-four hours at a temperature averaging near to 800° of mixtures containing originally equal weights of zinc and lead with varying proportions of tin:—

Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
0	98.70	1.30	0	1.57	98.43	0
7.01	89.87	3.12	9.28	5.39	85.33	2.27
12.77	82.98	4.25	16.36	8.00	75.64	3.59
19.29	73.17	7.54	21.56	10.04	68.40	2.27
22.84	65.80	11.36	23.94	11.39	64.67	1.10
27.12	54.98	17.90	26.62	12.13	61.25	-0.50
29.47	50.07	20.46	28.37	12.95	58.68	-1.10
31.66	45.74	22.60

FIG. 1.

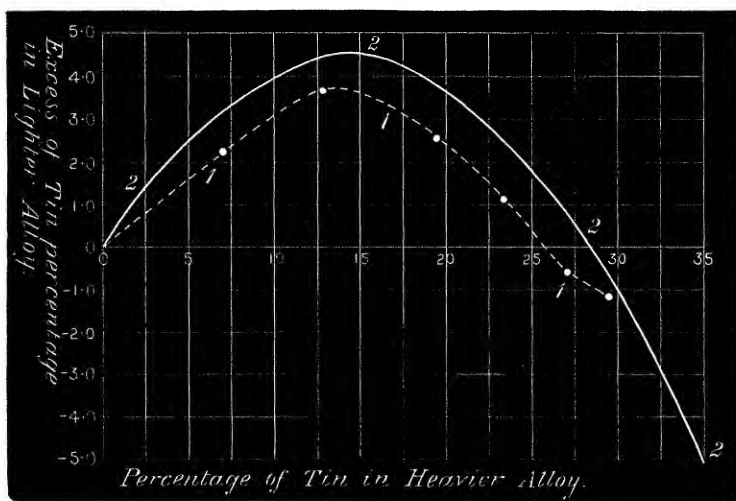


Fig. 1 represents the curve illustrating the tin distribution derived from these figures, the numbers in the first column being plotted as abscissæ and those in the last as ordinates (No. 1); the corresponding mean curve deduced from the observations at lower temperatures

(averaging near 650°), described in Part I, being represented by No. 2, in each case equal quantities of lead and zinc and varying proportions of tin being employed for the mixtures originally fused. The effect of the higher temperature is apparently to give a curve somewhat underlying that obtained at the lower temperature, and crossing the base line sooner; but the difference is not extremely great, and is probably at least partly due to the circumstance that the greater volatilisation of zinc at the higher temperature causes the proportion of lead relatively to zinc in the entire mass to rise higher: as shown in Part I, the tin distribution curve obtained with two parts of lead to one of zinc in the original mixtures underlies that obtained with equal proportions of the two metals, and crosses the base line sooner.

When the percentages of tin and zinc in the heavier alloys are plotted as abscissæ and ordinates respectively, a curve is obtained sensibly *overlying* that previously obtained at about 650° ; and similarly with the curve obtained by plotting the percentages of tin and lead in the lighter alloys as abscissæ and ordinates respectively.

The following tables exhibit the solubility values deduced from the mean curves thus graphically obtained, the corresponding values for 650° being annexed for the sake of comparison:—*

Solubility of Zinc in Lead-Tin.

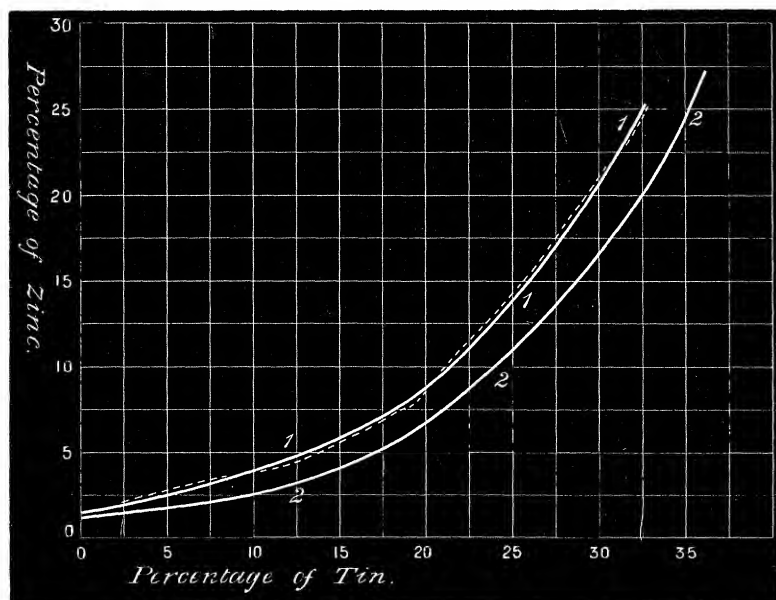
Per cent. of tin.	Temperature near 650° .		Temperature near 800° .	
	Per cent. of zinc.	Difference.	Per cent. of zinc.	Difference.
0	1.24		1.30	
2	1.44	0.20	1.80	0.50
4	1.65	0.21	2.30	0.50
6	1.89	0.24	2.80	0.50
8	2.15	0.26	3.30	0.50
10	2.45	0.30	3.80	0.50
12	2.85	0.40	4.40	0.60
14	3.4	0.55	5.10	0.70
16	4.1	0.7	5.9	0.80
18	5.0	0.9	6.9	1.00
20	6.1	1.1	8.1	1.2
22	7.5	1.4	9.6	1.5
24	9.25	1.75	11.6	2.0
26	11.4	2.15	14.1	2.5
28	13.9	2.5	17.1	3.0
30	16.7	2.8	20.4	3.3
32	19.8	3.1	24.0	3.6
34	23.2	3.4
36	27.0	3.8

* By inadvertence, some numerical inaccuracies exist in the table of solubility of

Solubility of Lead in Zinc-Tin.

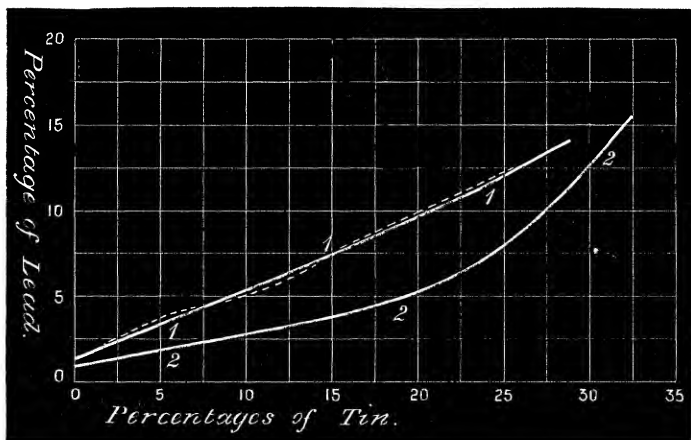
Per cent. of tin.	Temperature near 650°.		Temperature near 800°.	
	Per cent. of lead.	Difference.	Per cent. of lead.	Difference.
0	1·14		1·57	
2	1·47	0·33	2·35	0·78
4	1·80	0·33	3·15	0·80
6	2·13	0·33	3·95	0·80
8	2·46	0·33	4·75	0·80
10	2·80	0·34	5·55	0·80
12	3·14	0·34	6·35	0·80
14	3·50	0·36	7·15	0·80
16	3·9	0·40	7·95	0·80
18	4·5	0·6	8·75	0·80
20	5·3	0·8	9·55	0·80
22	6·3	1·0	10·35	0·80
24	7·5	1·2	11·20	0·85
26	8·9	1·4	12·05	0·85
28	10·6	1·7	12·90	0·85
30	12·75	2·15
32	15·5	2·75

FIG. 2.



zinc in lead-tin given in Part I for the abscissæ values (tin percentages) 26 and upwards; the corrected figures are given above.

FIG. 3.



Figs. 2 and 3 represent these values respectively, the curves marked 2 being those obtained at the lower temperatures (near 650°), and those marked 1 being the corresponding higher temperature mean curves (near 800°); the dotted lines being those connecting the points actually observed at near 800° .

Mixtures of Lead, Zinc, and Silver.

Owing to the lesser degree of fusibility exhibited by some of these mixtures, it was found necessary to employ throughout a temperature ranging between 750° and 850° , and generally pretty close to 800° . It is well known that on adding zinc to melted argentiferous lead the zinc rises to the top, carrying most of the silver present with it along with a little lead; whence, evidently, the curve representing the distribution of silver between the lighter and heavier alloys formed resembles that obtained with lead, zinc, and tin alloys when the proportion of tin present is but small, *i.e.*, the curve at first ascends above the base line; but no information appears to be extant giving any clue as to whether this kind of distribution would also be observed with mixtures containing large proportions of silver, or whether such mixtures would behave like lead-zinc-tin mixtures containing large proportions of tin, *i.e.*, furnishing a curve descending again to, and finally dropping below, the base line.

The analysis of the lead-zinc-silver alloys formed was made as follows:—a weighed quantity, usually some 5 or 6 grams, was dissolved in nitric acid and the solution diluted with so much hot water that on adding enough dilute hydrochloric acid to precipitate all the

silver present no lead chloride separated. The turbid liquid was kept hot in the water-bath for an hour or two, until the silver chloride had subsided, and was then filtered hot, the silver chloride being boiled up two or three times with water to wash out any lead chloride that might possibly have separated. The filtrate was evaporated with pure sulphuric acid in excess, and the lead sulphate formed separated and determined in the usual way. As with the lead-zinc-tin alloys described in Part I, it was found necessary to precipitate the zinc contained in the filtrate from the lead sulphate as sulphide, and to redissolve this (after filtration) in hydrochloric acid and precipitate whilst boiling as carbonate by sodium carbonate, finally weighing as ZnO; if the precipitation as sulphide were omitted, sensibly too high values were obtained from the presence of *lime*, presumably derived from the glass and porcelain vessels used. The ZnO, after weighing, was dissolved in hydrochloric acid and supersaturated with ammonia, and the trifling precipitate of alumina and ferric oxide (derived from the crucibles and clay test-tubes) estimated and subtracted. The figures given below are in all cases calculated upon the sum of the silver, lead, and zinc thus found

Series I.—Time of Fusion, 8 hours. Temp., 750—850°.

Percentage of silver in mixture before fusion.	Heavier alloy.			Lighter alloy.			Excess of silver percentage in lighter alloy over that in heavier.
	Silver.	Lead.	Zinc.	Silver.	Lead.	Zinc.	
0	0	98·70	1·30	0	1·57	98·43	0
3	0·02	98·25	1·73	5·75	1·95	92·30	5·73
6	0·12	98·36	1·52	12·32	5·12	82·56	12·20
9	0·34	97·16	2·50	17·23	9·00	73·77	16·89
10	0·18	97·67	2·15	18·96	8·62	72·42	18·78
12	0·19	97·39	2·42	20·95	11·81	67·24	20·76
14	0·37	97·81	1·82	24·10	9·06	66·84	23·73
16	0·60	96·55	2·85	28·85	7·34	63·81	28·25
18	0·85	97·23	1·92	33·77	3·04	63·19	32·92
20	1·19	95·46	3·35	34·86	2·83	62·31	33·67
22·5	1·38	96·40	2·22	38·33	2·78	58·93	36·95
25	1·61	96·00	2·39	39·95	2·86	57·19	38·34
27·5	1·82	95·73	2·45	41·90	3·27	54·83	40·08
31	2·52	95·10	2·38	46·43	3·66	49·91	43·91
36	3·01	95·59	1·40	53·74	3·70	42·56	50·73
38	3·58	95·23	1·19	54·15	3·53	42·32	50·57
41	5·30	93·47	1·23	56·67	4·32	39·01	51·37
44	8·31	90·12	1·57	60·13	7·06	32·81	51·82
47·5	11·45	86·70	1·85	62·94	9·54	27·52	51·49
52·5	14·06	84·10	1·84	65·48	10·50	24·02	51·42
57·5	17·14	80·43	2·43	66·19	12·85	20·96	49·05
62·5	19·45	77·62	2·93	66·24	14·78	18·98	46·79
65	67·39	16·66	15·95	..

Series II.—Time of Fusion, 24 hours. Temp., 750°—850°.

Percentage of silver in mixture before fusion.	Heavier alloy.			Lighter alloy.			Excess of silver percentage in lighter alloy over that in heavier.
	Silver.	Lead.	Zinc.	Silver.	Lead.	Zinc.	
0	0	98·70	1·30	0	1·57	98·43	0
5	0·02	98·64	1·34	9·34	2·51	88·15	9·32
7·5	0·10	98·38	1·52	15·46	4·63	79·91	15·36
10	0·32	97·61	2·07	22·07	6·96	70·97	21·75
12·5	0·25	97·08	2·67	22·28	7·56	70·16	22·03
15	0·88	96·23	2·89	27·95	6·17	65·88	27·07
20	1·12	96·98	1·90	39·49	3·46	57·05	38·37
25	1·46	96·58	1·96	41·82	3·90	54·28	40·36
27·5	1·60	97·14	1·26	48·11	3·46	48·43	46·51
30	2·26	96·46	1·28	48·93	3·82	47·25	46·67
35	5·35	93·27	1·38	51·86	4·47	43·67	46·51
40	7·78	90·76	1·46	53·98	4·78	41·24	46·20
45	9·36	88·62	2·02	61·07	7·23	31·70	51·71
50	10·75	86·95	2·30	61·93	10·28	27·79	51·18
60	68·89	18·28	12·83	..

(after correction) as 100. In the case of the lighter alloys, where zinc was the main constituent, as a rule the silver and lead only were determined, and the zinc taken by difference; but with the heavier alloys the zinc was invariably directly determined.

Series I is derived from the examination of thirty-eight compound ingots, and Series II from seventeen, several of the analyses quoted being the mean compositions derived from two mixtures nearly alike. The average loss by volatilisation and oxidation was about 4 grams out of 50—60 = about 8 per cent., in Series I, and 6 or 7 grams = about 13 per cent., in Series II, the zinc being the metal chiefly affected.

On plotting these figures as curves, it is noticeable, firstly, that the distribution of silver between the two alloys formed is such as throughout to yield a curve overlying the base line, and exhibiting a rise to a maximum, and subsequent slight fall. Thus curves 1 and 2, fig. 4, represent the numbers in Series I and II respectively, the percentages of silver in the *lighter* alloys being here taken as abscissæ, and the figures in the last column as ordinates.

Next, the curves obtained by plotting the percentages of silver and lead in the lighter alloys as abscissæ and ordinates respectively are most remarkable (curves 1 and 2, fig. 5). At first the two curves do not coincide, but they present the same general feature of rising to a first maximum, and then falling again to a point but little above the starting level, after which the two do not differ from one another

FIG. 4.

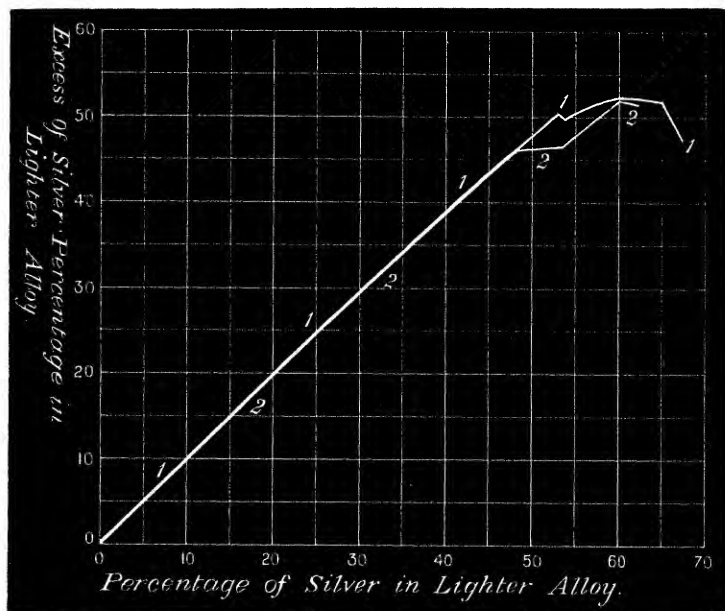
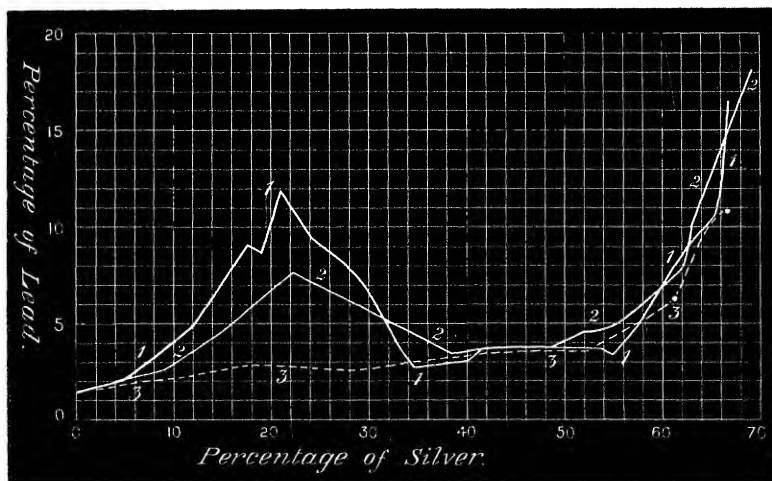


FIG. 5



by amounts outside the limits of variation ascribable to unavoidable differences of average temperature and fluctuations of temperature in the several experiments, both rising slowly until a point is reached when a very marked change takes place in the rate of ascent.

It is especially noticeable that the position of the first maximum is in each case close to that when the ratio between silver and zinc in the alloy is indicated by the formula AgZn_5 —

	Silver.	Zinc.	Lead.	Ratio of zinc to silver.
Series I.....	20·95	67·24	11·81	1 to 0·313
Series II.....	22·28	70·16	7·56	1 „ 0·317
Calculated for AgZn_5				1 „ 0·332
„ AgZn_4				1 „ 0·277

Further, the points where the rate of ascent suddenly becomes much more rapid are in neither case far from that indicated by the formula Ag_4Zn_5 —

	Silver.	Zinc.	Lead.	Ratio of zinc to silver.
Series I, between.... {	53·74	42·56	3·70	1 to 1·26
	56·67	39·01	4·32	1 „ 1·45
	Mean			1 „ 1·325
Series II, about	53·98	41·24	4·78	1 „ 1·31
Calculated for Ag_4Zn_5				1 „ 1·33
„ AgZn				1 „ 1·66
„ Ag_2Zn_3				1 „ 1·11

As regards these points, it is remarkable that alloys where upwards of nine-tenths of the whole consists of silver and zinc in the proportion Ag_4Zn_5 exhibit a distinct coppery red hue when a recently filed or polished surface is exposed to the air for a short time. As the proportion of Ag_4Zn_5 present diminishes owing to the presence of excess of silver, or of zinc, or of either with additional lead, the red colour becomes less marked, the tint being only a pale yellow, or even entirely white, when the alloys contain less silver and more zinc, or more silver and less zinc, than about the limits—

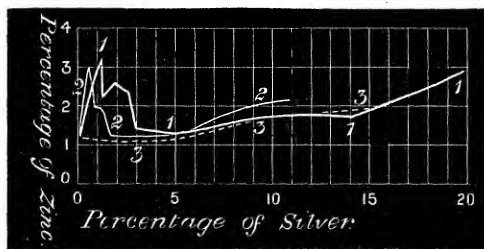
Silver	42 per cent.	62 per cent.
Lead	3 „	10 „
Zinc	55 „	28 „
	<hr/> 100		<hr/> 100

corresponding with a percentage of Ag_4Zn_5 of about 73 in the first case and 65 in the second.

It is further remarkable that mixtures of bismuth, zinc, and silver, on standing fused for some eight hours, separate into different ternary alloys, the lighter of which yield curves exhibiting exactly the same peculiarities as those above mentioned, viz., rise to maximum near AgZn_5 , fall again to a minimum, and then a slower rise again to Ag_4Zn_5 , marked by a red colour. These alloys will be discussed in a subsequent paper.

Thirdly, the curves obtained by plotting the percentages of silver in the heavier alloys as abscissæ and those of zinc as ordinates (Nos. 1 and 2, fig. 6) are in each case such as to indicate that, as long

FIG. 6.



as the mixture of metals used contains less than about 41 per cent. of silver in the first case and 28 in the second, the heavier alloy that separates invariably contains more zinc than that formed either when no silver at all is present, or when these limiting proportions are reached. At these limiting proportions the percentage of zinc present is slightly *lower* than that found in binary zinc alloy, as also is the proportion of zinc calculated per unit of lead, thus—

	Silver.	Zinc.	Lead.	Ratio of lead to zinc.
Binary alloy	0	1.30	98.70	1 to 0.0132
Series II	1.60	1.26	97.14	1 „ 0.0130
Series I	3.58	1.19	95.23	1 „ 0.0125

The lowering is so small that it might readily be attributed to experimental errors, were it not that a precisely similar and much more strongly marked result is obtained with alloys of silver, zinc, and bismuth, as will be shown in a future paper.

After these limiting proportions are passed the amount of zinc

present increases with the silver present, giving sensibly the same curve in each series.

The above results obviously lead to the conclusion that silver and zinc form at least two definite compounds, viz., AgZn_5 and Ag_4Zn_5 : the first of these can dissolve lead more freely than can either pure zinc or the second; so that when the silver and zinc are contained in the lighter alloy in exactly the proportion AgZn_5 , the lead dissolved is a maximum. Moreover, it results conversely that lead can dissolve AgZn_5 more freely than either pure zinc or Ag_4Zn_5 , so that, when circumstances favour the production of the first compound, the zinc dissolved in the heavier alloy is notably increased. It would seem that the compound Ag_4Zn_5 is so much less soluble than AgZn_5 that lead saturated therewith contains actually less zinc than when saturated with pure zinc; for the experiments with bismuth-silver-zinc alloys show that the zinc contained in the heavier alloys (calculated per unit of bismuth) gradually diminishes to a minimum as the silver present increases, and then regularly increases again, the position of this minimum being sensibly that where the silver and zinc present are in the proportion Ag_4Zn_5 . This point will be discussed in a future paper.

When more silver is present relatively to zinc than corresponds with Ag_4Zn_5 , then this compound is dissolved by lead, and conversely can itself dissolve lead, the more freely the more surplus silver is present; so that a more or less rapid rise in each solubility curve is observable when the silver present exceeds that requisite to form Ag_4Zn_5 with the zinc present.

The difference between the lighter alloy curves obtained in Series I and II leads to the remarkable conclusion that, when the compound AgZn_5 (containing dissolved lead) is kept fused for some hours, it tends to break up (presumably into free zinc and Ag_4Zn_5), and thereby to throw out of solution more or less of the dissolved lead; so that after 24 hours' fusion less lead is present in the lighter alloy than after only eight hours' fusion. Obviously, if it were practicable to effect this decomposition absolutely completely, the lighter alloy formed would be simply a mixture of Ag_4Zn_5 and more or less surplus zinc, saturated with lead; and hence the curve traced out with silver as abscissa and lead as ordinate should rise regularly from the origin up to the point where Ag_4Zn_5 without surplus zinc is present.

Owing to the volatility of zinc, we were unable to carry out any experiments with a view to tracing out such a regular curve, by maintaining the alloys in a fused state for lengthened periods of time (several days); but we succeeded in effecting the same object by the simple device of eliminating the lead that separated (along with some silver and zinc) on keeping the solution of lead in AgZn_5

fused for some time, so as to remove it from the sphere of action, and thus facilitate the separation in the same kind of way that removing the products of decomposition *pari passu* with their formation facilitates the decomposition by heat or the dissociation of ordinary chemical compounds.

After various trials, we found that the simplest way of effecting this was to prepare a series of mixtures of equal weights of lead and zinc and varying quantities of silver, and keep them fused for about eight hours, as in Series I; the compound ingots thus obtained were then cut in two, and the lighter portions fused separately without stirring for another period of eight hours, so as to be out of contact with the heavier portions formed during the first fusion. Similarly, the heavier portions were also fused separately. The result of this treatment was that each lighter portion underwent a further separation into a small quantity of heavy alloy and a much larger quantity of a lighter one; and, conversely, each heavier portion similarly separated into a small quantity of lighter alloy, which floated, and a much larger amount of heavier alloy. On repeating the operation, by cutting off the small quantity of heavy alloy (or lighter) that had thus separated, and fusing again for another eight hours, *no further separation to any material extent occurred* in the generality of cases, indicating that the limit of decomposition by fusion had been reached. Thus, for example, the following figures were obtained in two experiments with the lighter portions of the ingots first formed:—

Composition.	Silver.	Lead.	Zinc.
After first fusion for 8 hours.....	14·65	8·30	77·05
„ second „	16·93	2·64	80·43
„ third „	17·60	2·89	79·51
Mean of last two results	17·27	2·76	79·97
After first fusion for 8 hours.....	24·10	9·06	66·84
„ second „	27·37	2·66	69·97
„ third „	28·85	2·71	68·44
Mean of last two results	28·11	2·68	69·21

Similar results were obtained in various other cases; moreover, we found that, if instead of weighing up equal quantities of zinc and lead and a given proportion of silver, and fusing for eight hours, and then separating the two crude alloys formed, and again fusing the lighter alloy, a mixture of the three metals was made in about

the proportions representing those due to any given point on the earlier portion of curve No. 1, fig. 5, and kept in a state of fusion for eight hours or more, just the same effect was produced; *i.e.*, a small quantity of heavy alloy subsided, leaving a lighter alloy, *the composition of which was not altered materially by cutting off the separated heavy alloy and fusing again for eight hours more.*

Uniting together all the observations thus made, we obtained the following series of figures, representing the limiting compositions of the normal lighter alloys formed, *i.e.*, the compositions below which no further reduction in lead percentage could be obtained by keeping in a fused state for several hours longer:—

Series III.—Limiting Composition of Lighter Alloys.

Silver.	Lead.	Zinc.
11·51	2·37	86·12
17·27	2·76	79·97
24·49	2·65	72·86
28·11	2·68	69·21
37·54	3·14	59·32
46·23	3·56	50·21
52·78	3·60	43·62
61·12	6·40	32·48
64·58	10·00	25·42
66·25	10·84	22·91

On plotting these figures it is obvious that they give a curve (No. 3, fig. 5, dotted line) sensibly identical as regards its latter part with the corresponding portions of the curves obtained from Series I and II, the differences in no case being greater than the amounts that may reasonably be ascribed to unavoidable differences in the average temperature and in the small temperature fluctuations in the different experiments. But the first part of the curve is wholly different, the rise to a maximum at AgZn_5 and subsequent fall being wholly eliminated, and a regular ascent being visible instead, precisely as should be the case were the compound AgZn_5 wholly decomposed in each case, so that no excess of lead could be taken into solution over and above that due to the normal solubility in the particular mixture of silver and zinc (or of Ag_4Zn_5 and surplus zinc or silver) present. In similar fashion, we found that if the bottom portions of the compound ingots obtained after eight hours' fusion, and containing unduly high percentages of zinc, were cut off, and fused again separately for another period of eight hours, a small quantity of lighter alloy rose to the top, whilst the heavier alloy formed after the second fusion gave, on analysis, percentages of zinc and silver yielding a perfectly regular curve, instead of the abnormal

results obtained in Series I and II with mixtures of metals containing less than 28—41 per cent. of silver, and yielding heavier alloys after the first fusion, containing less than 5 or 6 per cent. of silver.

Series IV.—Limiting Compositions of Heavier Alloys.

Silver.	Lead.	Zinc.
0·38	98·33	1·29
0·75	97·98	1·27
1·52	97·30	1·18
4·03	94·72	1·25
8·44	90·00	1·56
11·09	87·20	1·71
14·82	83·25	1·93

The dotted curve No. 3, fig. 6, represents these values, which obviously imply that the method of treatment adopted had, as with the lighter alloys, sufficed to decompose completely the compound AgZn_5 originally present, and hence to prevent any larger proportion of zinc being present than that due to the normal solubility in lead of Ag_4Zn_5 mixed with free zinc, in the case of the alloys earliest in the series, or to the solubility in lead containing surplus silver of the compound Ag_4Zn_5 , in those occurring later in the series.

The following tables are derived from all the foregoing results, excepting the earlier alloys of Series I and II, where excess of lead was present in the lighter alloy, or of zinc in the heavier one, owing to the presence of undecomposed AgZn_5 ; they represent the mean composition of the zinc-lead-silver alloys, producible under such conditions that no AgZn_5 is present to increase the amount of zinc contained in the heavier, and of lead in the lighter, alloys respectively:—

Solubility of zinc in lead-silver.			Solubility of lead in zinc-silver.		
Percentage of silver.	Percentage of zinc.	Difference for 1 per cent.	Percentage of silver.	Percentage of lead.	Difference for 1 per cent.
0	1·30		0	1·57	
1	1·25	-0·05	10	1·97	0·040
2	1·20	-0·05	20	2·37	0·040
3	1·20	0	30	2·77	0·040
4	1·22	+0·02	35	3·00	0·046
5	1·24	+0·02	40	3·25	0·050
6	1·26	+0·02	45	3·55	0·06
7	1·28	+0·02	50	3·90	0·07
8	1·32	0·04	51	3·97	0·07
9	1·38	0·06	52	4·04	0·07
10	1·46	0·08	53	4·12	0·08
11	1·56	0·10	54	4·20	0·08
12	1·68	0·12	55	4·35	0·15
13	1·81	0·13	56	4·60	0·25
14	1·95	0·14	57	5·00	0·40
15	2·10	0·15	58	5·5	0·5
16	2·26	0·16	59	6·1	0·6
17	2·43	0·17	60	6·8	0·7
18	2·61	0·18	61	7·55	0·75
19	2·80	0·19	62	8·35	0·8
20	3·00	0·20	63	9·2	0·85
			64	10·1	0·9
			65	11·1	1·0
			66	12·5	1·4
			67	14·5	2·0
			68	17·5	3·0

On comparing together the relative effects on the solubility of lead in zinc, and zinc in lead, produced by the presence of tin and silver respectively, it is at once obvious that if 100 parts of zinc can take up m parts of lead in presence of x parts of a third metal (tin or silver), or if 100 of lead can take up n parts of zinc in presence of x of the third metal, then m and n are invariably much greater when the third metal is tin than when silver, even if the solubility in presence of tin be reckoned at only 650° C., or thereabouts, instead of 800°.

Thus the following tables are calculated from the mean solubility curves previously described, giving the correlated values of x , m , and n for the three cases—tin at about 650°, tin at about 800°, and silver at about 800°:—

x .	Zinc dissolved by 100 parts of lead in presence of x parts of tin (or silver).				Lead dissolved by 100 parts of zinc in presence of x parts of tin (or silver).			
	Tin at 650°.		Tin at 800°.		Tin at 650°.		Tin at 800°.	
	n .	Diff.	n .	Diff.	m .	Diff.	m .	Diff.
0	1.25	..	1.32	..	1.15	..	1.60	..
5	1.90	0.65	2.60	1.28	2.05	0.90	1.85	0.25
10	2.55	0.65	4.00	1.40	2.95	0.90	2.10	0.25
15	3.6	1.05	5.55	1.55	3.85	0.90	2.35	0.25
20	5.1	1.5	7.35	1.80	4.90	1.05	2.60	0.25
25	7.2	2.1	9.70	2.35	6.4	1.5	2.85	0.25
30	9.9	2.7	12.6	2.9	8.4	2.0	3.10	0.25
35	13.3	3.4	16.2	3.6	10.9	2.5	3.35	0.25
40	17.1	3.8	20.3	4.1	13.8	2.9	3.60	0.25
45	21.2	4.1	24.9	4.6	17.0	3.2	3.85	0.25
50	25.6	4.4	29.8	4.9	20.6	3.6	4.10	0.25
55	30.2	4.6	35.0	5.2	24.5	3.9	4.40	0.30
60	34.9	4.7	40.4	5.4	28.7	4.2	4.70	0.30
65	39.7	4.8	45.9	5.5	5.05	0.35
70	44.6	4.9	51.5	5.6	5.40	0.35
75	49.6	5.0	57.2	5.7	5.80	0.40
80	54.7	5.1	6.20	0.40
85	59.8	5.1	6.60	0.40
90	65.0	5.2	7.00	0.40
95	70.3	5.3	7.40	0.40
100	75.6	5.3	7.80	0.40

FIG. 7.

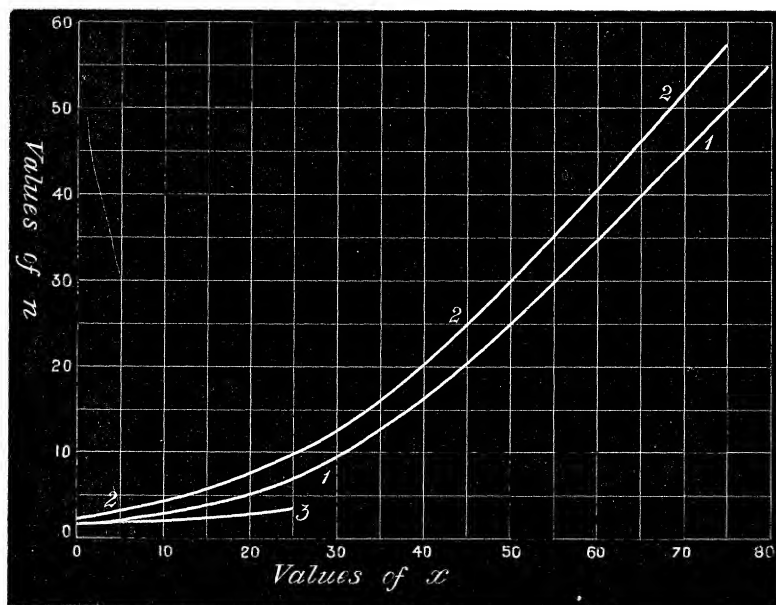
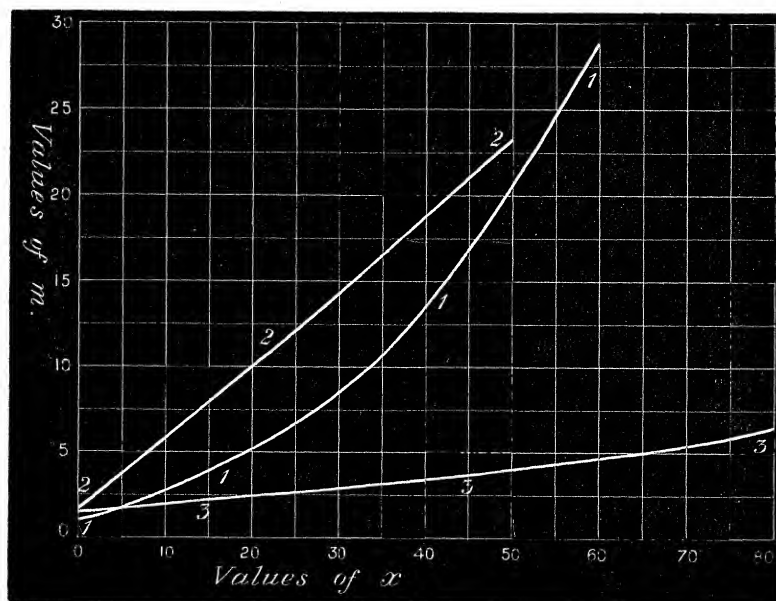


FIG. 8.



Figs. 7 and 8 represent these values of x , n , and m , respectively, the curves marked 1 being those obtained with tin at 650° ; those marked 2 with tin at 800° ; and those marked 3 with silver at 800° ; the value of x being abscissæ, and those of m and n ordinates.

We have much pleasure in acknowledging the assistance afforded us by Mr. T. M. Wyatt in carrying out a considerable portion of the analytical results above detailed.

II. "Experiments on Vapour-density." By E. P. PERMAN, B.Sc., Clothworkers' Exhibitioner at University College, London. Communicated by Professor RAMSAY, F.R.S. Received April 17, 1890.

The Vapour-density of Bromine.

The main purpose of my work on this subject was to discover if bromine had any tendency to dissociate at low pressures, *i.e.*, down to about 15 mm. of mercury, and at moderate temperatures.

The subject was suggested by Professor Ramsay, to whom I am greatly indebted for constant advice and assistance in carrying out the work. The method adopted for determining the vapour-densities was a modification of the Dumas method, from which it differed in three essential points:—(1) The globe was not immersed in a bath, but had a vapour-jacket. (2) The weight of the vapour in the globe was not found by direct weighing, but by running in an absorbent liquid, and estimating it volumetrically. (3) A series of vapour-density determinations at different pressures was made with the same quantity of vapour by lowering the pressure, absorbing the vapour drawn off and estimating its quantity.

As to previous work on this subject, Jahn has shown ('Wien, Akad. Sitzber.,' vol. 85, 2. Abth., 1882, p. 778) that the vapour-density becomes normal at about 230° ; Meier and Züblin ('Deutsch. Chem. Ges. Berichte,' vol. 13, 1880, p. 405) and Crafts ('Comptes Rendus,' vol. 90, 1880, p. 183) have shown that partial dissociation takes place at very high temperatures; and Professor J. J. Thomson states that "vapour-density determinations showed that bromine vapour is dissociated if it is heated for a long time at a low pressure, even though the temperature is not very high" ('Roy. Soc. Proc.,' vol. 42, 1887, p. 345). His chief results are:—

FIG. 1.

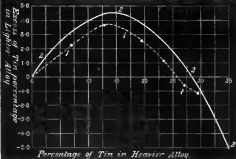


FIG. 2.

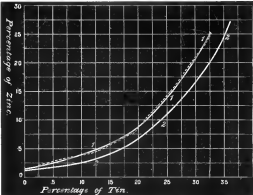


FIG. 3.

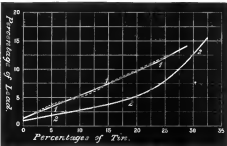


FIG. 4.

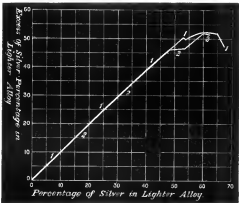


FIG. 5

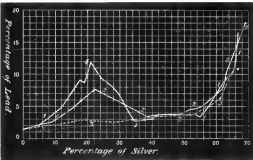


FIG. 6.

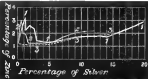


FIG. 7.

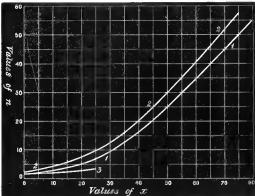


FIG. 8.

